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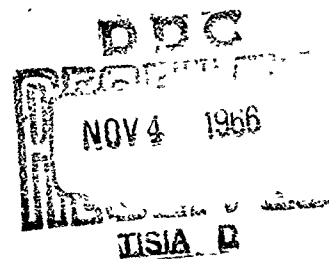
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Amendm. No. 4

The Attack of Zinc Monocrystals by Strong Acids and Surface  
Disintegration of the Dissolving Metal

by

M.E. Straumanis and Y. Wang



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The Attack of Zinc Monocrystals by Strong Acids and Surface  
Disintegration of the Dissolving Metal

M.E. Straumanis and Y. Wang

Abstract

The attack of Zn monocrystals by acids ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$  and  $\text{HNO}_3$ ) was studied. Crystals of high purity (99.999%) as well as those containing small amounts (0.01 to 0.05% by weight) of Al, Mg and Au were used. The crystals planes behaved very similarly in the first 3 acids: the (0001) planes were attacked perpendicularly, the dissolution process penetrated to a depth of 4 to 8 microns, then spread laterally; followed by renewed penetration. In this way the attack of the (0001) plane continued. In more concentrated acids (around 5N) the bottom of the etch pits became smooth, resisting further attack of the acid, before the next layer was penetrated. Branched, very fine material, consisting of pure Zn remained at some sites in the form of elevations on the surface of the dissolving crystalline planes (surface disintegration). Often hexagonal and sometimes dihexagonal etch pits could be observed on the (0001) plane. The attack of the (10 $\bar{1}$ 0) plane in dilute acids occurred by penetration into the depth between several basal planes. Irregular etch pits were formed. In more concentrated acids, the (10 $\bar{1}$ 0) plane shifted parallel to itself, leaving piles of branched material behind at places. More striations (parallel to 0001) were formed on (11 $\bar{2}$ 0) planes. The attack of the pyramidal planes was similar. Strong  $\text{HNO}_3$

worked like an electropolisher. To explain the various dissolution phenomena, and formation of etch pits, the presence of a protective film on the monocrystal surfaces, as for electropolishing had to be assumed. There was no evidence for the assumption that etch pits are formed at dislocations. Al and Mg present in the crystals did not influence their dissolution to any degree in contrast to Au, which covered the crystal faces in form of a dark Au-Zn alloy, thus, stimulating the crystallographic dissolution.

#### Introduction

Many studies have been performed in order to clarify the etching behavior of zinc and the formation of etch pits on its polished surface. However, most of the work has been done on polycrystalline material. Single zinc crystals have been rarely used. It was found in such cases that there are only a few faces which develop on the surface of a Zn monocrystal during the etching process: mainly the basal (0001), the prismatic (10 $\bar{1}$ 0) and the pyramidal plane (12 $\bar{1}$ 6) which shift parallel to themselves during the etching process. All other planes are attacked so that one or two or more of the mentioned planes remain; steps are, therefore, formed<sup>1</sup>. As a consequence, the electrochemical equilibrium potential on all (etched) Zn crystal surfaces is the same.<sup>2,3</sup>

Later, to mention only a few investigations, the formation of etch pits in relation to dislocations was studied by Servi<sup>4</sup>, Gilman<sup>5</sup> and George<sup>6</sup>. Bassi and Hugo produced etch pits on

polycrystalline Zn by etching it after electrolytic polishing.<sup>7</sup> Bicelli and Rivolto investigated the etch pits formed on (0001) and (11 $\bar{2}$ 0) planes.<sup>8</sup>

The problem of the attack of Zn by acids, its anodic dissolution in relation to the deviation from Faraday's law came into another phase, when it was found by James and Stoner<sup>9</sup> that in addition to etching, there is evidence for surface disintegration of the metal. Disintegration of a metal during dissolution into very small particles was first shown for Be.<sup>10</sup> The same occurs also during anodic dissolution of Mg<sup>11</sup>, Ga<sup>12</sup>, Fe<sup>13</sup>, and In<sup>14</sup> in acids or neutral solutions.

The attack of Zn single crystals was studied mainly in dilute acids. In view of that it was interesting to have answers to the following questions: 1. In what manner are the various faces of Zn monocrystals attacked by strong acids at low, moderate, and high concentrations? 2. Is there a difference in attack by various acids? 3. Can disintegration phenomena be observed even in concentrated acids? 4. What is the influence of impurities? 5. What is the mechanism of disintegration? The subject of the present report is to provide answers for these five questions.

#### The Materials, Preparation and Cutting of Zn Monocrystals

For the growth of single crystals, three kinds of Zn were used: 1. Sticks of 99.99% purity (from Fisher Scientific Company), 2. high purity rods (99.99+%) from the American Smelting and Refining Company and 3. Zn splatters of still

higher purity (99.999+%) from the same company. The main impurities were Cu, Fe, and Pb. The 99.99+% Zn contained also some Ag (0.0002%).

The alloying elements, to introduce certain impurities into the monocrystals, were Al, Mg and Au which all were about 99.99% pure. The chemicals used (HCl, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, HNO<sub>3</sub>, etc.) were of reagent grade.

The monocrystals were grown by the Bridgman method<sup>15</sup>, by lowering the metal sample, which was vacuum sealed in a pyrex tubing, through a furnace (heated to 500°C) by means of a clock mechanism with a speed of 1 cm/hr. The crystals obtained were up to 5 cm long and 0.9 to 1.4 cm in diameter.

For the growth of alloy crystals 1% or 2% master alloys were prepared first. The proper amounts of Zn and of Al, Mg or Au were weighed, placed in a pyrex tubing, which then was evacuated and sealed. The whole was heated at 500°C for 72 hours and shaken twice a day. The master alloys were then used for the preparation of the dilute Al-, Mg- and Au-Zn alloys. The weighed amounts were heated in vacuum sealed pyrex tubes at 500°C for 48 hours and shaken twice per day. All the samples were furnace cooled. Then the alloys were sectioned, polished and etched to be sure that no segregation of the alloying elements were present.

The alloy crystals were grown in the same way as the pure Zn crystals. Monocrystals containing 0.005, 0.025 and 0.05% b.w. of Al, 0.005, 0.01 and 0.025% Mg and 0.01, 0.02 and 0.04% b.w. Au were obtained.

All the monocrystals could easily be cleaved along their basal (0001) planes after they were cooled in liquid nitrogen.

In order to cut the cylinders (having parallel basal planes at their ends) in certain other crystallographic directions without deformation, an etch cutter was used. The cutter was built by Reitsma according to the description published by Yamamoto and Watanabe<sup>16</sup>. 8N HNO<sub>3</sub> was used as a cutting solution. The time required for cutting a single crystal of 9 mm in diameter was about one hour. As the cut surface was slightly ragged, it was gently ground on 0, 2/0, 3/0 and 4/0 emery paper. After grinding the deformed surface layer was removed by etching. Four crystallographic planes were used for etching and disintegration observations: the (0001) - without cutting, the prismatic plane of first order (10 $\bar{1}$ 0), that of the second order (11 $\bar{2}$ 0) and a pyramidal plane (01 $\bar{1}$ L). The cuts through the crystals are shown in the schematic Fig. 1 and could be made with a precision of  $\pm 3^\circ$ .

#### Chemical and Electrolytic Etching

The chemical etching was performed by immersing clean Zn monocrystals, having the desired crystallographic planes, into the etching solution for a certain period of time. Then the specimens were washed, dried and observed under a Reichert microscope, using mainly high magnification (achieved with oil immersion objectives). The oil was then removed from the sample surface by wiping it with acetone.

Prior to anodic etching, the respective surface of each crystal had to be very clean and smooth. The unexposed surface was insulated with wax and the electrolytic circuit used



is shown in Fig. 4 of reference 12. The circuit was closed before the anode was immersed. To stop etching, both electrodes were taken out of the electrolyte, the circuit opened, and the electrodes immersed into distilled water. Usually, the anodic etching time varied from a few seconds to several minutes. The current density was adjusted from a lower to a higher value.

### The Experimental Results

a. The basal plane. Before etching the basal planes (on sections cleaved from the crystals along 0001), they were examined for smoothness with the interference tester of the microscope in monochromatic light obtained by a filter. The presence of regular, concentric interference fringes indicated that the basal plane was very even, mirrorlike (Fig. 2). Steps could easily be seen (Fig. 3) as well as twin strips (Fig. 4). However, all these samples were suitable for etching.

The pure Zn monocrystals without exception were very resistive against the action of 2 N HCl. To produce some etch pits, a Pt needle was pressed to the (0001) plane of the Zn crystal within the acid. The (0001) plane became slightly etched; however, etch pits in the form of approximate hexagons frequently appeared in the vicinity of the needle, which acted as a local cathode. The etch pits were very shallow and small (Fig. 5). The formation of regular hexagonal etch pits was rare.

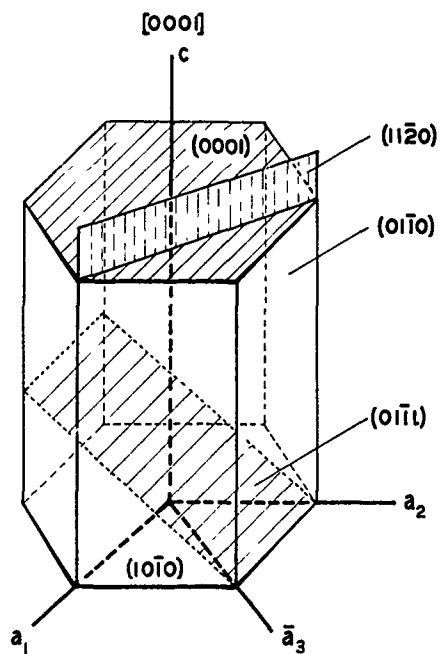


Fig. 1  
The cuts laid through the Zn monocrystals.

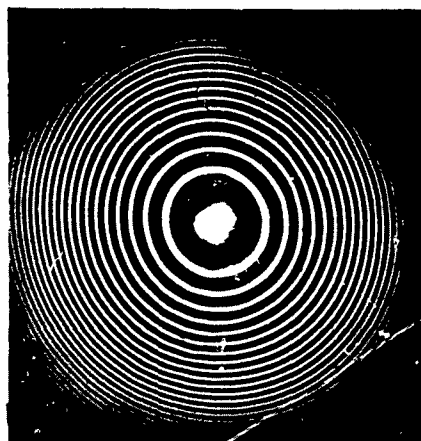


Fig. 2  
Interference fringes on a  $(0001)$  plane of a Zn crystal containing 0.005% Mg. Unetched. 165x.



Fig. 3  
Step, 0.00015 mm. high on the  $(0001)$  plane of the crystal, Fig. 2.



Fig. 4  
Twin strip on the  $(0001)$  plane of a Zn crystal containing 0.0005% Al. 165x.

Increasing the concentration of HCl up to 6 N, a typical "leaves" etching pattern resulted in only 10 seconds (Fig. 6). By prolonging the etch time up to 80 seconds deeply etched surfaces were obtained (Fig. 7). Interference patterns showed that the white areas were quite even. The dark portions, however, were much higher, and upon focusing the microscope on them, mountainlike peaks could be observed (Fig. 8).

These black ridges displayed peaks about 7.5 microns above the even, white reflective areas.

HCl of a still higher concentration produced a "branched" etching pattern, shown in Fig. 9. Again the black branches and areas were ridges and the large white areas were lower, as if electropolished, but covered with black dots. If the same crystal was etched with concentrated HCl (12 N), many hexagonal pits appeared, with some black material collected in the centers of the hexagons. The pits showed lateral "steps" descending to the bottom of the pits (Fig. 10). Sometimes even dihexagonal etch pits could be detected with plenty of black material in their centers (Fig. 11). This dark material was easily removable by wiping. Upon etching, the crystal surface of the same sample (Fig. 11) with concentrated HCl for 15 sec., its surface became smooth and shining in a violent reaction. It was, however, covered in a thin layer with some loose black material. Upon wiping with wet cotton, some of the black particles could be removed, but some remained sticking to the surface of the specimen. Nearly perfect but slightly

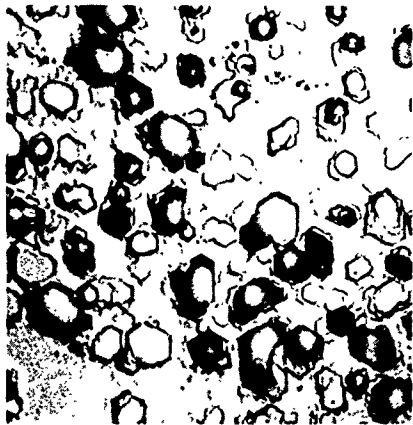


Fig. 5  
(0001) of a Zn monocrystal (99.999+ pure) etched in 2 N HCl for 20 sec. touching it with a Pt needle. 750x.

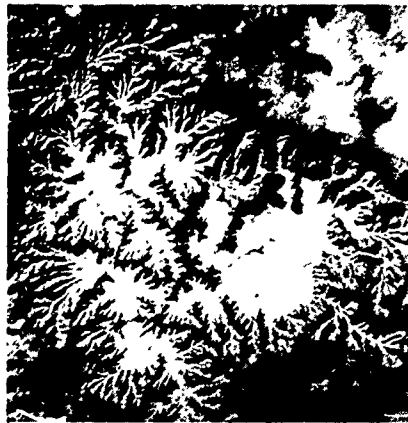


Fig. 6  
(0001) of 99.99% Zn etched in 6 N HCl for 10 sec. 1430x.

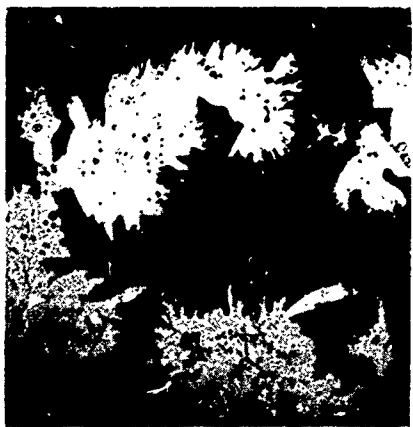


Fig. 7  
(0001) of the same crystal etched in 6 N HCl for 80 sec. Dark areas represent elevations. 750x.



Fig. 8  
Mountain peaks (7.5 micron high) above the white, even areas of Fig. 7. 750x.

elevated, shiny hexagons could be observed under the microscope (Fig. 12), thus representing "negative" etch pits.

It was necessary to clarify the nature of the black material appearing in the etch pits and composing the black ridges (see Fig. 7, 8, 9, 10 and 11). A section through a 99.99+% Zn rod was made and etched with 12 N HCl for one minute and washed. The dark material appearing on the section was removed from the surface of the dry metal by a piece of Scotch tape. Black and shiny particles could be visualized under the microscope on the tape even at low magnification. Observed with an oil immersion objective in transparent light all the particles appeared completely opaque and no salt particles could be recognized. In the light of a vertical illuminator shiny metallic particles resembling those of Zn could clearly be recognized. Unfortunately, the amount of black particles was too small to make an x-ray identification picture. However, as the amount of the black material could not be accumulated by prolonged etching, as it evidently dissolved, it, therefore, consisted of Zn powder formed during the dissolution by partial disintegration of the surface metal.

No such phenomena could be observed by etching the (0001) plane of Zn in HNO<sub>3</sub> (9.5 N). Even in 5 seconds the surface of the crystal became so shiny that it appeared electropolished. However, large but shallow etch pits (Fig. 13) could be found at some spots of the mirrorlike (0001) surface.



Fig. 9  
(0001) plane of 99.999+% Zn monocrystal  
etched in 9 N HCl for 15 sec. 750x.

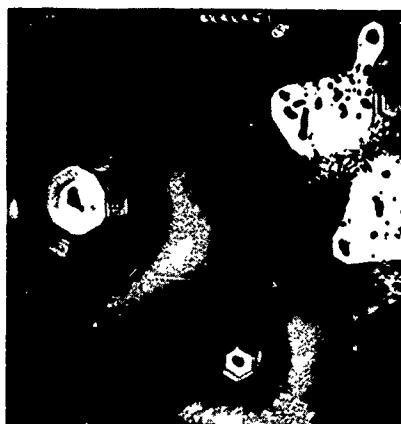


Fig. 10  
Etch pits on a (0001) plane of 99.999+% Zn  
monocrystal etched in 12 N HCl for 10 sec.  
750x.



Fig. 11  
Etch pits on a (0001) plane of a 99.99+% Zn  
monocrystal etched in 9 N HCl for 20 sec.  
1430x.

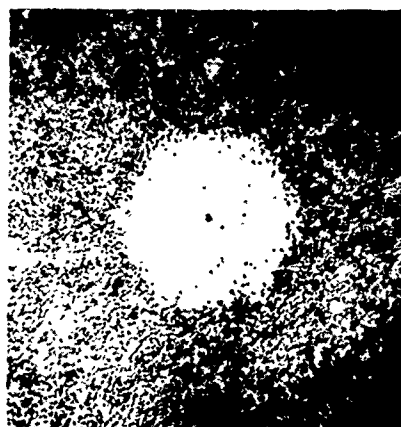


Fig. 12  
Negative etch pit on the (0001) plane of  
the crystal Fig. 11 etched for 15 sec. in  
12 N HCl. 1430x.

The behavior of Zn monocrystals containing small amounts of metals less noble than Zn itself, e.g., Al and Mg in etching solutions was very similar to that of pure Zn. 2 N HCl produced small etch pits, which distorted only slightly the smooth 0001 surface, as shown by the interference picture (Fig. 14). However, treating the same crystal with 12 N HCl for 10 seconds, the surface remained shiny but became uneven, as a very irregular fringe pattern appeared (Fig. 15). Nevertheless, the bottom of the hexagonal (Fig. 15a) but mostly round etch pits (Fig. 15b) was even, judging from the interference patterns.

It was interesting to note that the twin strips (Fig. 16) on the (0001) plane were not as much attacked as the plane itself.

Upon etching the (0001) planes of the Zn-Al crystals in 12 N HCl, a black material as shown in Fig. 10 could also be observed.

The Zn monocrystals containing Mg behaved similarly. Deformation twin strips were less attacked than the crystal itself. Upon etching with concentrated HCl for 10 and 20 seconds consecutively, the black branches on the shiny base appeared. As in the case of Zn-Al, the branches were elevations (Fig. 17). For prolonged etching, even in less concentrated HCl, the deformation strips were also attacked, black ridges appeared, but because of the very even and large patches of (0001) planes developed, the crystal surface appeared shiny (Fig. 18). When the same crystal was treated for 5 more seconds in concentrated

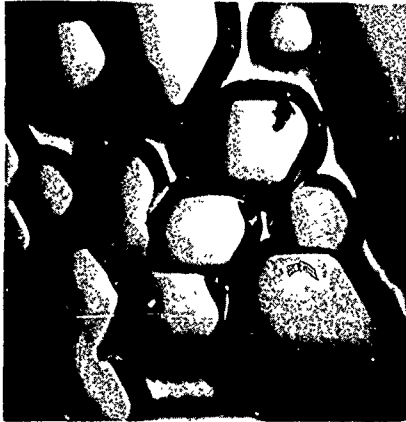


Fig. 13  
(0001) plane of a 99.99% Zn monocrystal etched in 9.5 N HNO<sub>3</sub> for 5 sec. Bottom of the etch pits. 750x.



Fig. 14  
(0001) plane of a Zn - 0.025% Al monocrystal, etched in 2 N HCl for 20 sec. Interference pattern. Depth of the pits  $\sim 0.00015$  mm. 165x



Fig. 15 a and b  
(0001) plane of a Zn - 0.025% Al monocrystal, etched in 12 N HCl for 5 to 10 sec. Interference patterns. 165x.

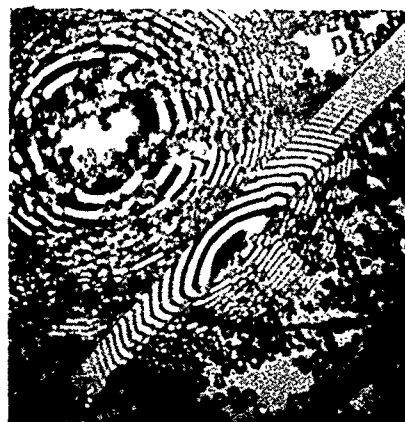


Fig. 16  
(0001) plane of a Zn - 0.05% Al monocrystal, etched in 2 N HCl for 20 sec. Interference pattern. 165x.



HCl, the ridges disappeared and the surface became nearly mirrorlike. The Au in Zn-Au monocrystals, upon etching the latter, remained on the metallic surface and covered it to a smaller or larger extent. Hence, shorter etching times had to be used in order to observe the attacked metallic surface. Hexagonal etch pits with rounded edges could frequently be observed (Fig. 19), when the (0001) face was treated with  $\text{HNO}_3$  (9.5 N) for a short time (3 sec.); the etch pits were similar to those previously described (see Fig. 13). Dilute HCl (2 N) worked differently in producing irregular etch pits with dark, rounded edges, especially when the Au content of the crystal was increased (Fig. 20). Again there is a similarity with Figs. 7, 9, and 18. The dark regions represent ridges. More concentrated HCl (6 N) produced cleaner surfaces with large and deep etch pits. Fig. 21 shows the basal plane and the bottom of the etch pits; the depth of the latter was about 4.5 microns. Upon increasing the amount of Au (up to 0.04%) a dark, Au-containing layer is formed during the etching of the crystal, which usually cracked at some places and revealed a shiny background.

b. The prismatic planes. Both first and second order planes (see Fig. 1) of the crystals were used for the etching experiments. Fig. 22 shows the (10 $\bar{1}$ 0) plane of a single crystal etched with 6 N HCl for a comparatively long time of 85 seconds. The picture is typical for the respective planes of all pure Zn crystals, etched with HCl. Horizontal lines, parallel

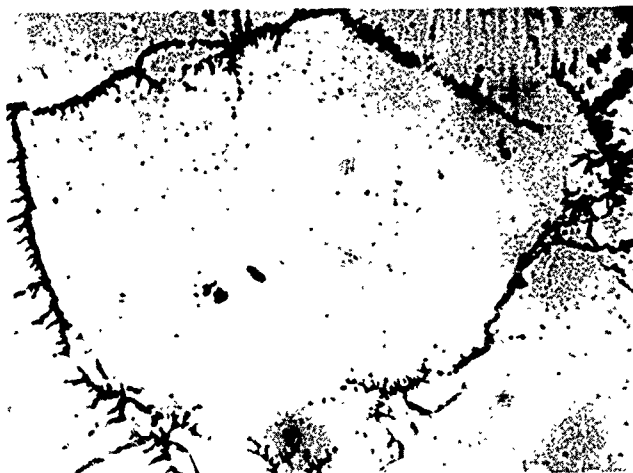


Fig. 17  
(0001) plane of a Zn - 0.005% Mg monocrystal,  
etched in 12 N HCl for 10 sec. 1430x.

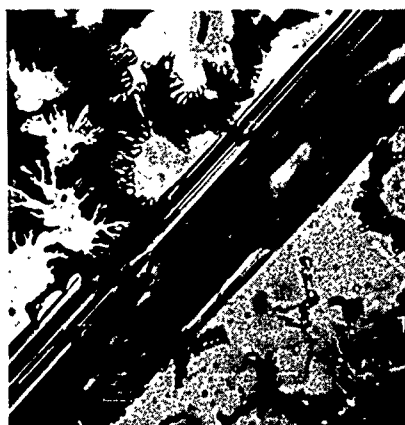


Fig. 18  
(0001) plane of a Zn - 0.01% Mg monocrystal,  
etched in 6 N HCl for 30 sec. 1430x.



Fig. 19  
(0001) face of a Zn - 0.01% Au monocrystal,  
etched in 9.5 N HNO<sub>3</sub> for 3 sec. 750x.

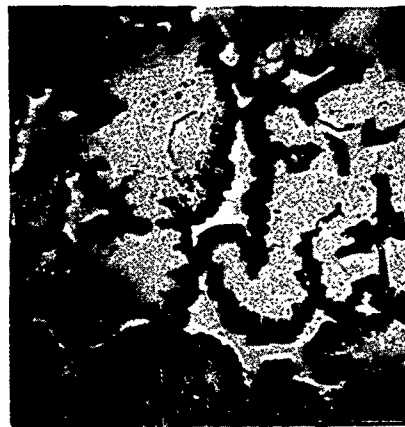


Fig. 20  
(0001) face of a Zn - 0.02% Au monocrystal,  
etched in 2 N HCl for 20 sec. 750x.

to the 0001 plane, can readily be seen. The broad zigzag lines under various angles to the horizontal ones represent ridges. They are higher than the white even parts, similarly as shown by Figs. 7, 9, 18 and 20 and consist of disintegrated Zn. Etching the same planes with dilute HCl (2 N) for a still longer time (5 min.), rare but large, deep, and irregular etch pits, stretched in the direction of the parallel striations were observed. The etching process penetrated into the depth of the crystal in between the basal planes (Fig. 23). Concentrated HCl developed large V-shaped pits with pyramidal planes constituting the wall of the pits (Fig. 24).

8 N HNO<sub>3</sub> produced etch patterns very similar to those obtained in HCl (Fig. 22), only the crystal surface was smoother and no ridged zigzag lines were observed. However, some disintegrated material was accumulated along the elevated, dark, parallel lines.

The (10 $\bar{1}$ 0) plane of single Zn crystals containing Al and Mg was more easily attacked by HCl than that of pure Zn monocrystals. Generally the same striations parallel to (0001) as shown in Fig. 22 were formed on the (10 $\bar{1}$ 0) plane of the alloy crystals. The dark striations represented ridges consisting of some disintegrated material. Still more of the latter was observed when Al-containing Zn crystals were strongly etched with concentrated HCl: etch pits with dark material in their centers were observed (Fig. 25, for comparison see Fig. 10 and 11).



Fig. 21

(0001) face of a Zn - 0.02% Au monocrystal,  
etched in 6 N HCl for 5 sec. 1430x.  
above - the etched 0001-plane  
below - bottom of the etch pits.



Fig. 22

(10 $\bar{1}$ 0) plane of a 99.999% Zn monocrystal,  
etched in 6 N HCl for 85 sec. 750x.



Fig. 23

(10 $\bar{1}$ 0) plane of a 99.999% Zn monocrystal,  
etched in 2 N HCl for 5 min. Deep etch  
pits. 1430x.

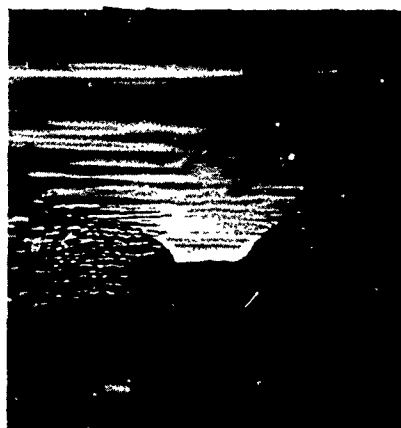


Fig. 24

(10 $\bar{1}$ 0) plane of a 99.999% Zn monocrystal,  
etched in 12 N HCl for 10 sec. V-shaped  
etch pit. 1430x.

Zn monocrystals containing Au reacted faster with 2 N HCl: dark material accumulated on the entire  $(10\bar{1}0)$  surface. However, white horizontal bands similar to those shown in Fig. 22, running parallel to the basal plane, could easily be distinguished under the microscope. The dark brown material was removed from a strongly etched  $(10\bar{1}0)$  surface of a monocrystal (containing 0.02% Au) by a piece of Scotch tape and observed under the reflecting light of a microscope: particles with metallic lustre could easily be distinguished. To identify the nature of the particles, deposits obtained by strong etching of the crystal surfaces with 1 N HCl, were removed, then washed dried and used for the x-ray examination. Only weak Au lines were present on the powder patterns in addition to other broad lines which could not be identified, but in all probability belonged to a Zn and Au alloy. Thus, the dark material on the surface of single crystals contained considerable amounts of Zn<sup>17</sup>.

The etch patterns on the second order prismatic planes (Fig. 1) were similar to those obtained on the first order. A crystal of 99.999+% Zn was cut parallel to the  $(11\bar{2}0)$  plane and etched with 9 N HCl for 25 seconds. Striations which run parallel to the basal plane were developed; however, they were more or less curved. In 8 N HNO<sub>3</sub>, shallow, large and very irregular etch pits, having shiny curved walls and bottoms were developed. The surface was less smooth than in the case of (0001). The  $(11\bar{2}0)$  planes of the alloy crystals were not examined.

c. The pyramidal planes. The fourth crystallographic plane (Fig. 1) used for etching was the  $(01\bar{1}2)$ . Usually dark striations parallel to the basal plane were developed also on it, very much resembling Fig. 22. Upon prolonged etching of a 99.999+% pure Zn crystal in 9 N HCl, black particles and concentrations of them were scattered throughout the  $(01\bar{1}2)$  surface. All these places were higher than the white and glossy strips (Fig. 26). The pyramidal planes of the Zn alloy monocrystals were not investigated.

d. Anodic etching in acids. It was of further interest to know whether anodic etching in acids would work in the same way in the absence of any current. For this purpose, a single crystal electrode served as an anode while a Pt electrode was used as a cathode. Of course, to see the influence of the current only dilute acids could be chosen as electrolytes (0.5 - 2 N HCl,  $H_2SO_4$ ,  $HClO_4$  and  $HNO_3$ ). At times, more concentrated acids were also used.

The (0001) plane of a single Zn crystal was subjected to currents higher than usually used in electropolishing: 1000 ma/cm<sup>2</sup> for 10 seconds. Etch grooves on a generally very even surface were developed which formed with each other angles of about 60 and 120° (Fig. 27). On the bottom of the grooves there was some black material (Fig. 28) which consisted, if observed under high magnification, of minute shiny metallic particles, in all probability Zn. The depth of the grooves was ~5.5 microns. No black material developed on the



Fig. 25

(10 $\bar{1}$ 0) plane of a Zn - 0.05% Al monocrystal, etched in 12 N HCl for 5 sec. Etch pits with dark centers. 750x.

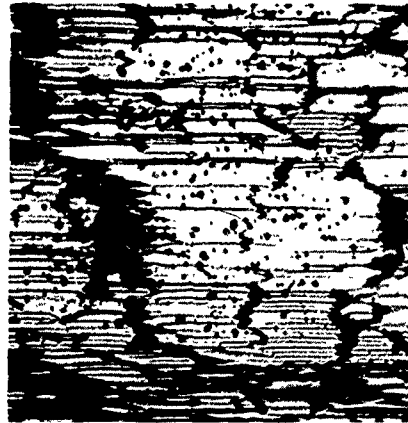


Fig. 26

(01 $\bar{1}$ 1) plane of a 99.999+% pure Zn monocrystal, etched in 9 N HCl for 2 min. Dark places, lines and spots are elevations. 750x.

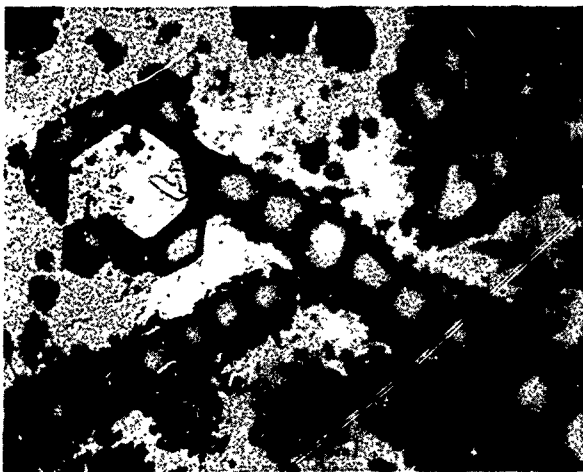


Fig. 27

(0001) plane of a 99.99% pure Zn monocrystal, etched anodically in 2 N HCl for 10 sec; 1000 ma cm<sup>2</sup>. Upper level of the surface. 575x.



Fig. 28

The same crystal surface shown in Fig. 27. Bottom of the etch grooves. Black material Fig. 7. 575x.

anodes during the electrolysis in  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$  and  $\text{HNO}_3$ , the anodes became more or less shiny. Deep etch pits were formed in dilute  $\text{HClO}_4$  on the quite even basal plane (Fig. 29).

In the more concentrated acid, separate hexagonal etch pits could be observed.  $\text{HNO}_3$ , as in the case of free etching, produced shiny surfaces, especially when the acid was more concentrated (9.5 N). It is very possible that in such cases, the chemical action overshadowed the anodic dissolution.

The prismatic plane ( $10\bar{1}0$ ) of the crystal of Fig. 27 was etched under the conditions mentioned for 15 seconds (see Fig. 30).

On the shiny surface, the attacked locations were in the form of striations which ran parallel to the basal plane. Upon further anodic etching at higher current densities up to  $1.5 \text{ amp cm}^{-2}$  for 75 seconds, black particles accumulated on the surface of the crystal, and the horizontal lines appeared still more clearly. A larger amount of black particles accumulated on the ( $11\bar{2}0$ ) face of the etched sample under the same conditions. In case of a ( $01\bar{1}l$ ) plane, groups of black particles appeared on the surface of the plane after etching it at  $1 \text{ amp cm}^{-2}$  for 1 minute. Striations, although curved but generally parallel to the basal plane could readily be seen on the ( $11\bar{2}0$ ) as well as on the ( $01\bar{1}l$ ) planes.

These anodic etching experiments show that on the polished as well as on the even surfaces formed during the anodic etching process (by "electropolishing"), there is a film present which resists to a certain degree the action of the acid and



protects the metal underneath. Only at higher current densities, can this layer be destroyed at the weaker spots and there the etching process is somehow determined by the structure of the metal. In fact, electropolishing is easily explained on the basis of a resistive film forming during anodic dissolution.<sup>18</sup>

#### Discussion and Conclusions

It follows from all the experimental data that some protective layers must be present not only on polished and electropolished samples but also on single crystal surfaces. As the (0001) plane of Zn could be produced by cleaving the crystal rods at low temperatures, no rough mechanical treatment was involved, and therefore, impurities or severe distortions were not introduced into the crystals. On the other hand, there are no absolutely pure metals and Zn, even the purest, contains metallic impurities, of which the most active ones are those of low H-overpotential (Cu, Fe and Pt in respective dilute alloys). Since such atoms and their accumulations must also be present on the crystal surface planes, a single crystal surface, such as (0001) of Zn must be attacked uniformly by even dilute strong acids. But this is not the case. Such crystal surfaces are very resistive against the action of acids. However, if the plane is contacted with a Pt needle the latter becomes a cathode, the protective film, which in all probability consists of some oxides breaks down at the weakest places due to the impact of ions going into solution.

On such spots, the etching process can start and propagate in directions as determined by the symmetry of the crystal surface (crystallographic dissolution). Thus on the (0001) plane of Zn, hexagonal-like etch pits will appear frequently. From here the dissolution process can spread laterally aided by the accumulations of impurity metal atom concentrations, uncovered during the dissolution.

Views have been expressed that impurity atoms concentrate along dislocation lines and etch pits appear where such lines cross the surface<sup>19</sup>. In view of the observations accumulated, this role of dislocations in the formation of etch pits can be questioned. Every aqueous corrosion process, especially in acids, starts with the formation of etch pits. The number of them per surface unit increases with increasing amounts of active impurities (having a low H-overpotential) and so does the rate of corrosion as clearly was shown for Al<sup>20</sup>. If dislocations are responsible for the formation of etch pits, then it follows that the density of dislocations should increase with the amount of impurities. This is a conclusion which has not yet been proved. Furthermore, dislocations can be introduced into metals by deformation or cold work. One has, therefore, to expect that during and after that treatment, the impurities still present in the metal will diffuse to the many dislocations and hence, increase the number of etch pits and also the rate of corrosion. However, experience reveals that this is not so. For instance, Fig. 16 shows that deformation twins are more resistive with regard to etch pit

formation than the neighborhood, although this may not always be correct.

Deformed metals do not exhibit an increased rate of dissolution, as proven with Al<sup>21</sup> and with Fe by Foroulis and Uhlig<sup>22</sup>. If the impurity atoms concentrate themselves around dislocations, one should expect that during the formation of the etch pit, the former should become dispersed in the solution due to undermining. However, frequently heaps of a black substance can be observed in the center of the etch pits (see Figs. 10, 11 and 12). Then there is the question of concentration of impurity atoms around a dislocation. While the migration of a few atoms to the latter is understandable, the diffusion of large amounts against the concentration gradient seems to be out of question. Concentration of impurity atoms to clusters could, nevertheless, occur during the solidification of dilute alloys. It also seems doubtful whether a few impurity atoms are sufficient to produce an etch pit by local action. Fig. 10 and 11 show that large amounts of a metal that would act as a cathode, are necessary to form etch pits. At least it has to be admitted that impurity atom accumulations as such can also produce etch pits. Then, of course, etch pits to determine the number of dislocations, leads to false, exaggerated results.

Thus weak spots in the protective surface film which may be caused by impurity atom accumulations or imperfections in the crystal structure underneath the film are the starting points of etch pit formation. Once a pit is formed, the

dissolution continues, if not disturbed, crystallographically and in case of active metals - by local action.

The process of dissolution penetrates into the depth of the crystal and then laterally. In the case of the (0001) plane of Zn single crystals, the depth is between 4-8 microns. As can be seen from the interference patterns, the bottoms of the etch pits (Fig. 15a and b) are quite even, although in rare cases of hexagonal shape. The reason is the very fast action of the high concentrations of HCl, so that a number of etch pits overlap, producing an even bottom (Fig. 7, 9, 11, 17, 18 and 20) but corrugated (Fig. 7 and 18) lateral walls, which are black on the figures, and exhibit a slower rate of dissolution. Hence, the walls remain in the form of ridges. In all probability, because of their rough surface, they act as local cathodes, displaying a lower H-overvoltage. The centers of the etch pits (Fig. 10 and 11) may consist of such loose material. This black material may also be branched (Fig. 31, 7 and 8), parts of it may separate from the monocrystal in form of small particles due to the uneven action of the strong acid. This process constitutes the surface disintegration of the crystal. The small separated particles may dissolve in the acid. Thus, there are regions on the same metal surface, which are more or less resistive to the acid.

The reason the dissolution process penetrates into the crystal perpendicularly to (0001) only to a certain depth and then spreads laterally is explained by the layer-like structure of



Fig. 29  
(0001) plane of a 99.99% pure Zn monocrystal,  
etched anodically in 0.5 N  $\text{HClO}_4$  for 1.5 min;  
2000-2500  $\text{ma cm}^{-2}$ . 1430x.



Fig. 30  
(1010) plane of a 99.99% Zn monocrystal,  
etched anodically in 2 N  $\text{HCl}$  for 15 sec;  
1000  $\text{ma cm}^{-2}$ . 145x.

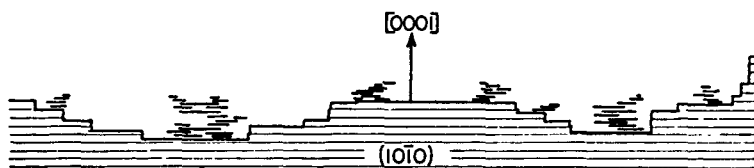


Fig. 31  
Attack of 0001 of Zn by strong acids ( $\text{HCl}$ ,  
 $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$ ) and surface disintegration of  
the crystal. Schematically.

the Zn monocrystals. The small amounts of Cd still present in the starting material (or the Al or Mg added to it) concentrates during the growth of the crystals in layers parallel to the basal plane. These layers, which seem to resist more the action of the acid are evenly spaced throughout the crystal.<sup>23</sup>

Consequently, etch pits produced on the plane perpendicular to (0001) have a different shape. For instance, the (10 $\bar{1}$ 0) plane which is artificial, and also covered with some kind of protective layer, is attacked by a diluted acid (HCl) at the weak spots of this layer (Fig. 23). Deep etch pits are produced, located between the more resistive parallel basal planes. Therefore, the etch pits become elongated in the direction of these planes.

More concentrated HCl (6 to 12 N) evidently destroys the protective layer on the whole surface exposed to the acid and the attack is therefore more even (Fig. 22) as for the pyramidal planes (Fig. 26). Black, roughened material (which is Zn) as well as the periodic structure which runs parallel to the basal plane can be seen readily on both pictures. However, in separate cases, V-shaped etch pits, limited by four stepped down walls, could also be observed (Fig. 24).

Since the metals Al and Mg are less noble than Zn, they do not stimulate the dissolution of Zn, but may go into solution first, if present in the Zn monocrystal. It also may be that the two metals are helpful in the production and stabilization of the periodic structure within the Zn monocrystals.

Gold is very active as a cathode because of its low H-overpotential. However, its activity if alloyed with Zn is decreased because the local Au cathodes produced are not pure. Thus, we have a Zn-Au alloy with an increased H-overpotential. Nevertheless, the surface of Zn monocrystals containing Au becomes dark upon etching because of the accumulation of Au-containing Zn particles remaining in contact with the crystal. In Fig. 20 the dark parts represent elevations and simultaneously the cathodic areas. Nevertheless, the etching process proceeds crystallographically as the bottom (the 0001 plane) becomes even and shiny, and frequently hexagonal etch pits are formed (Fig. 21). The process of dissolution proceeds, therefore, even in the presence of small amounts of Au, as described above.

The action of  $\text{HNO}_3$  is different because this acid acts as a strong oxidizer and evidently destroys the protective layer present on the monocrystals and in all probability produces a new one, but of different composition.  $\text{HNO}_3$  in a more concentrated form easily oxidizes the hydrogen developed on the surface of active metals; therefore, the action of impurities as local cathodes is significantly decreased. Hydrogen can develop at any place of the dissolving surface, as it is oxidized to  $\text{H}_2\text{O}$  and does not require spots of low H-overvoltage for its development. The dissolution is predominantly chemical (occurring at any spot of the exposed surface). Projected spots become leveled as the crystallographic dissolution is suppressed, and the etched surface looks electropolished<sup>18</sup>.

However, the remaining crystallographic dissolution may produce rare etch pits (for instance on 0001 as shown in Fig. 13 and 19) even in  $\text{HNO}_3$ .

Using anodic etching, deep pits, formed by crystallographic dissolution, appeared on the monocrystal anodes. For the explanation the presence of a protective film, on the single crystal surface appearing during electropolishing must be assumed.

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